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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Polymerization of Acetylenic Derivatives. XXVI. Polymerization of 9-Ethynylanthracene with Phosphinic, Arsinic, and Stibinic Initiators

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To cite this Article Simionescu, C. I. , Dumitrescu, Svetlana , Grigoras, M. and Negulescu, I.(1979) 'Polymerization of Acetylenic Derivatives. XXVI. Polymerization of 9-Ethynylanthracene with Phosphinic, Arsinic, and Stibinic Initiators', Journal of Macromolecular Science, Part A, 13: 2, 203 — 218

To link to this Article: DOI: 10.1080/00222337908066598

URL: http://dx.doi.org/10.1080/00222337908066598

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J. MACROMOL. SCI.–CHEM., A13(2), pp. 203-218 (1979)

Polymerization of Acetylenic Derivatives. XXVI.* Polymerization of 9-Ethynylanthracene with Phosphinic, Arsinic, and Stibinic Initiators

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ABSTRACT

9-Ethynylanthracene has been polymerized at 80°C by use of complex phosphinic, arsinic, and stibinic initiators, e. g., $NiCl_2 \cdot 2PPh_3$, and the obtained products have been divided into benzene-soluble and benzene-insoluble fractions. It has been shown that the benzene-insoluble polymer has a conjugated polyenic structure while the soluble polymer, with $\overline{M}$ less than 1500 daltons, contains dihydroanthracene units in the backbone in addition to the conjugated double bonds. It has been found that by using the above initiators the polymers are mainly cis. The cis to trans isomerization has been shown by DTA and DSC measurements to occur between 260 and 290°C.

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*For Part XXV, see C. I. Simionescu, Sv. Dumitrescu, and V. Percec, Polym. J., 8, 139 (1976).

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INTRODUCTION

The peculiar behavior of 9-vinylanthracene (9-VA) in polymerization reactions, i. e., the participation of carbon atoms 9 and 10 of the central ring in the reaction, raises the question of the polymerization ability of the acetylenic homolog, 9-ethynylanthracene (9-EA) and of the structure of the polymers formed.

Attempts to polymerize 9-VA with Ziegler catalysts were unsuccessful [1] and polymerizations of this monomer in presence of initiators usually used for anionic and cationic polymerization of common monomers led only to polymers of low molecular weight having the anthryl group inserted in the main chain [2-5]. This peculiarity could be explained on one hand by steric hindrance which occurs at the addition of the new unit to the growing chain and on the other hand by the high reactivity of the carbon atom 10 of the anthryl group which determines 9-VA to behave like a hexatriene.

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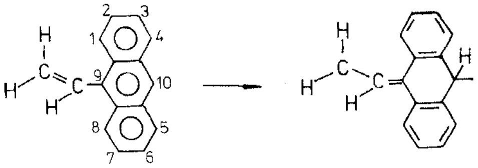
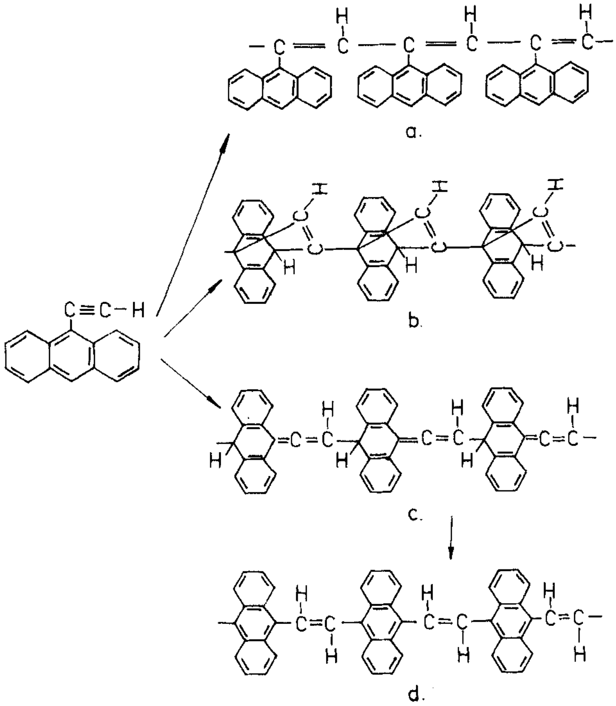


Similarly, by polymerization of 9-EA the following structures could be considered: (a) a linear polyene with pendent anthryl groups obtained by triple bond polymerization; (b) a Diels-Alder structure formed by successive cycloaddition of the ethynyl group of one monomer unit to carbon atoms 9 and 10 of another 9-EA molecule, and (c) an allenic carbon-containing backbone which by proton migration isomerization gives rise to (d) a poly-9,10-dimethineanthracene structure.

In addition to these four isomeric structures, the substituted polyene could theoretically appear both as cis or trans stereoisomer, each one having a cisoid or transoid enchainment [6-8]. The relative stability and the interconversion of these geometrical isomers are dependent on the synthesis conditions and subsequent treatment of polymers [9-11].

The present paper deals with the polymerization of 9-EA in presence of complex phosphinic, stibinic, and arsinic derivatives of group VIII transition elements and with the structure of the formed polymers.



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EXPERIMENTAL

9-EA was synthesized by chlorination of 9-acetylanthracene with PCl_5 in PCl_3 followed by dehydrochlorination of the obtained product (i. e., 9-α-chlorovinylanthracene) with $NaNH_2$ in liquid ammonia [12]. The crude monomer was transformed to its silver salt for storage. Pure 9-EA was obtained just prior to the use by decomposition of the silver salt with 2 N HCl followed by petroleum ether extraction and evaporation of the extract which was previously passed through an alumina column. The IR spectrum of 9-EA (Fig. 1a) exhibits two bands characteristic of the triple bond at 3250 cm^{-1} ($\nu_{\equiv C-H}$, strong) and 2100 cm^{-1} ($\nu_{C\equiv C}$, weak) and a couple of bands peculiar to substituted anthracene, e. g., at 730, 790, 850, and 895 cm^{-1}. 9-VA used as model derivative for polyenic structure of poly-9-ethynylanthracene (PEA) was synthesized according to the method reported by Hawkins [13].

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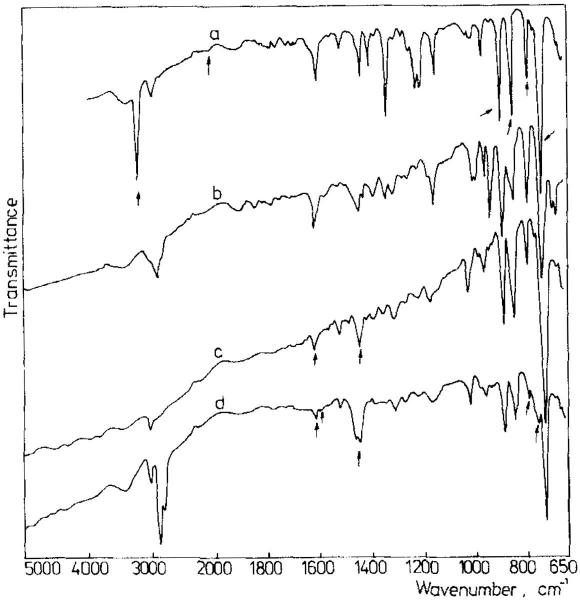

FIG. 1. IR spectra of: (a) 9-EA monomer (ether cast 9-EA on KbR pellet); (b) 9-VA monomer (KBr pellet); (c) PEA, insoluble fraction (KBr pellet); (d) PEA, soluble fraction (KBr pellet).

The following complexes were synthesized and investigated as potential initiators for polymerization of 9-EA: $NiCl_2 \cdot 2PPh_3$, $NiBr_2 \cdot 2PPh_3$, and $NiI_2 \cdot 2PPh_3$ [14]; $CoCl_2 \cdot 2PPh_3$ [15]; $RhCl \cdot 3PPh_3$ [16]; $PdCl_2 \cdot 2PPh_3$ [17]; $PtCl_2 \cdot 2PPh_3$ [18]; $PdCl_2 \cdot 2PPh_3$ [19]; $NiCl_2 \cdot 2PBu_3$ [20]; $PtCl_2 \cdot 2AsPh_3$, $PdCl_2 \cdot 2AsPh_3$, and $PdCl_2 \cdot 2SbPh_3$ [21].

Polymerization of 9-EA was carried out in glass ampoules at the reflux temperature of an ethyl alcohol-tetrahydrofuran mixture (90/10,v/v). After passing of the established reaction time (5 hr) the content of the ampoules was mixed with an equal volume of 5% HCl containing methanol. The precipitated material was then divided into a benzene-insoluble fraction (A) and a benzene-soluble (B) fraction, The molecular weight of fraction B was determined by cryoscopy in benzene. IR and UV spectra were recorded by using a Unicam SP 200 spectrometer and a Unicam SP 800B spectrometer, respectively. Thermogravimetric analyses were performed in air with a Paulik-Paulik Erdey (Budapest) thermobalance and DSC data were obtained in nitrogen (Perkin-Elmer DSC-1B).

TABLE 1. Polymerization of 9-EA with Complex Initiators[a]

Initiator	Yield (%)	Fraction A (%)[b]	Fraction B (%)[c]	M (dalton)[d]
$NiCl_2 \cdot 2PPh_3$	37.3	Traces	100.0	1480
$NiBr_2 \cdot 2PPh_3$	49.9	28.5	71.5	-
$NiI_2 \cdot 2PPh_3$	51.9	39.3	60.7	980
$CoCl_2 \cdot 2PPh_3$	23.2	Traces	100.0	1340
$RhCl \cdot 3PPh_3$	49.6	Traces	100.0	840
$PdCl_2 \cdot 2PPh_3$	37.3	27.3	72.7	1210
$PtCl_2 \cdot 2PPh_3$	37.0	12.4	87.6	750
$PdCl_2 \cdot 2PBu_3$	39.3	12.2	87.8	1370
$NiCl_2 \cdot 2PBu_3$	51.4	10.9	89.1	-
$PtCl_2 \cdot 2AsPh_3$	28.0	Traces	100.0	-
$PdCl_2 \cdot 2AsPh_3$	84.8	69.2	30.8	940
$PdCl_2 \cdot 2SbPh_3$	38.0	54.4	45.6	-

[a] Solvent: EtOH-THF (90/10,v/v), 5 ml; Monomer, 0.5 g; Initiators, 0.025 g; reflux temperature; time, 5 hrs.

[b] Fraction soluble in benzene.

[c] Fraction insoluble in benzene.

[d] Molecular weight cryoscopically determined in benzene.

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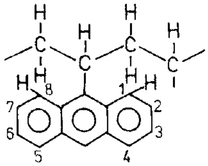
RESULTS AND DISCUSSION

Polymerization of 9-EA with Modified Ziegler Initiators

The data regarding the polymerization of 9-EA with modified Ziegler initiators of general formula $MtX_a \cdot bYZ_3$, where Mt is a transition metal of group VIII, i. e., Ni, Co, Rh, Pt, and Pd; X is Cl, Br, or I; Y is P, As, or Sb; Z is phenyl or n-butyl radical; A = 2 or 3 and b = 1 or 2, are listed together with the reaction conditions in Table 1. It can be seen that, unlike 9-VA which hardly polymerizes with Ziegler initiators [1], the acetylenic derivative gives polymers rather easily.

The attempts to build a Stuart-Brigleb model of the vinyl polymer showed that steric hindrance between hydrogen atoms 1 and 8 of the anthryl group and the hydrogen atoms of the main chain make it difficult to build poly-9VA of the head-to-tail type:



This hindrance could partially explain the inefficiency of Ziegler initiators in polymerization of 9-VA. PEA, having virtually no hydrogen atom to interfere with hydrogen atoms of carbon atoms 1 and 8, could easily acquire a regular structure. It will be shown in this paper that by polymerization of 9-EA with modified Ziegler initiators mentioned in Table 1 polymers of structure 1a are indeed preferentially formed.

The polymer yield is a function of the catalyst composition and decreases in the following order: Mt: Pd, Ni, Rh, Pt, Co; X: Cl, Br, I; Z: n-Bu, Ph.

Similarly to other arylacetylene polymers obtained with the same initiators, e. g., polyphenylacetylene [6], poly-α-ethynylnaphthalene [9], and poly-β-ethynylnaphthalene [18], PEA has a low degree of polymerization ($\overline{GP} \simeq 4$-7, fraction soluble in benzene). However, unlike these polymers which appear only as materials soluble in benzene, benzene-soluble PEA is accompanied by a dark insoluble fraction.

Useful information regarding the structure of 9-EA polymers could be obtained from their electronic spectra. UV absorption spectra of dihydroanthracene derivatives are different from anthracene derivatives because of the interruption of the conjugation in the central ring. Consequently, dihydroanthracene derivatives do not fluoresce and do not absorb at wavelengths higher than 300 nm [22, 23]. UV spectra of both soluble PEA and 9-VA (derivative taken as model for usual head-to-tail enchainment of 9-EA) exhibit distinct maxima in two regions of the spectrum assigned to the transition from the anthryl ring: a maximum centered between 250 and 260 nm and a plurality of peaks at longer wavelengths, i. e., between 325 and 390 nm (Fig. 2). The electronic spectrum of the polymer exhibits in the visible domain a large continuous absorption centered around 550 nm attributed to the $\pi \rightarrow \pi^*$ transition of chain electrons (Fig. 3). The similarity of UV spectra of 9-VA and of PEA is a prime hint

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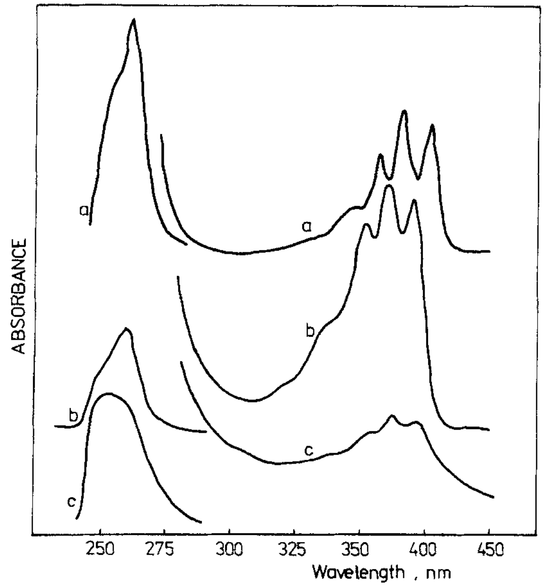
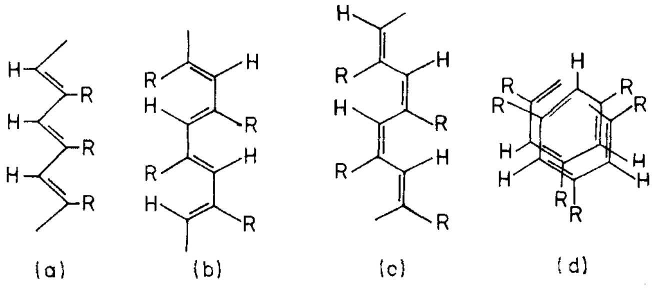
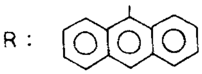


FIG. 2. Electronic spectra (UV range) of: (a) 9-EA monomer; (b) 9-VA monomer; (c) PEA, soluble fraction. Solvent, chloroform.





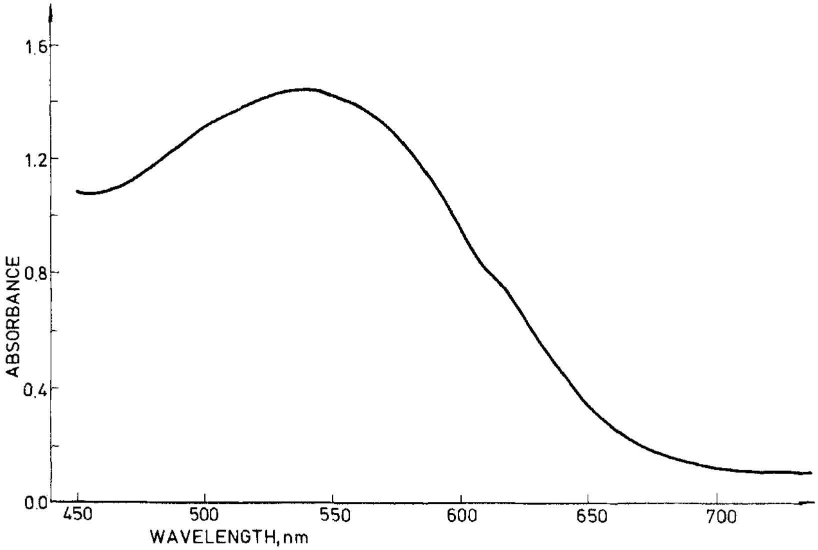


FIG. 3. Electronic spectrum (visible range) of PEA, soluble fraction. Solvent, chloroform.

that 9-EA polymers synthesized with this complex initiators have a conjugated polyenic structure.

However making a comparison between the extinction coefficients of the model (i. e., 9-VA, monomer) and PEA at nearly the same wavelength (Table 2), one can assume that the lower absorbance values of the polymer are mainly a consequence of the presence of dihydroanthracene units in the polymer chain. The major contributing factor to the bathochromic shift of UV absorption bands of 9-EA vs. 9-VA seems to be steric inhibition of resonance. The 9-EA molecule is planar and, therefore, resonance between the triple bond and the anthryl ring is at a maximum. In 9-VA the coplanar arrangement would be extremely crowded, and the anthryl group must be turned at a considerable angle to the plane of the triple bond in order to avoid excessive van der Waals repulsion. On the other hand, in comparison with the UV spectrum of 9-VA, the UV spectrum of the polymer exhibits a slight bathochromic shift of bands at large wavelengths and a hypsochromic shift of bands at small wavelengths. Similar effects were observed in the UV spectrum of poly-9-vinylacridine when compared with the UV spectrum of ethylacridine [24].

The characteristic absorption range of anthryl rings is well

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TABLE 2. Molar Extinction Coefficients at Different Wavelengths in Chloroform Solvent

Derivative	λ_{max} (nm)	$\epsilon_{max} \times 10^3$ (l./mole-cm)
9-EA	255	166
	265	240
	313	2.24
	348	4.47
	364	8.71
	382	12.1
	403	11
9-VA	260	159
	355	8.13
	372	8.52
	390	7.42
PEA	255	32.4
	360	5.89
	375	7.42
	394	7.08

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defined in the polymer spectrum (Fig. 2c) asserting an ordered arrangement of the pendent anthryl groups on the chain or part of it. A study of the molecular structure of PEA, particularly by using models, shows that anthracene rings considerably restrict the number of sterically feasible theoretical configurations of the chains. Possible structures require a twisted chain with pendent groups on the same side of the backbone similar to isotactic vinyl polymers (all cis or cis-cisoid arrangement) a more rigid structure similarly to a syndiotactic configuration (all trans or trans-transoid arrangement). These configurations could explain the hypsochromism in the absorption spectrum, and poor π-donor properties should be expected in comparison with model derivative, 9-VA, as only the terminal residues are readily accessible for complexing in a sandwich-type complex [24].

Substituted dihydroanthracene units could be identified in the IR spectrum of the polymer. The IR spectra of all 9-substituted anthracene derivatives exhibit a strong band around 730 cm^{-1} which was associated with the out-of-plane deformation vibration of C–H of carbon atoms C_1 and C_8. (For example, in unsubstituted anthracene this band appears at 727 cm^{-1}, but in 9-methoxyanthracene it is shifted to 734 cm^{-1} [25].) In 9,10-disubstituted anthracenes this band is shifted to 760 cm^{-1}. By comparing IR spectra of 9-EA and 9-VA and that of soluble and insoluble polymer fractions (Fig. 1) one can conclude that the polymerization took place through the opening of the triple bond, as the bands characteristic of the triple bond are absent, and the polymer spectra are roughly similar to that of the vinyl derivative. Noticeable differences, on the other hand, between IR spectrum of the soluble polymer fraction and the model derivative for the polyenic structure point to the presence of dihydroanthracene units in polymer: a new band at 760 cm^{-1} and a corresponding weakness of the band from 790 cm^{-1}, splitting of the band at 1450 cm^{-1} (deformation vibration of the C–H bond in position 10) and two new bands at 1590 cm^{-1} ($\nu_{C=C}$ of aromatic nuclei of dihydroanthracene units) and at 1620 cm^{-1} ($\nu_{C=C}$ of the polyenic backbone and anthracene ring).

Both soluble and insoluble polymer fractions are thermally stable up to 300°C. Above this temperature the degradation occurs in air or inert media (nitrogen).

Interconversion of Geometrical Isomers of PEA

Typical thermograms of PEA are shown in Fig. 4. One can see DTA curves exhibit an exothermal effect just before the degradation which starts at 160°C for the soluble polymer fraction and at 260°C for the insoluble polymer fraction. This effect was reinvestigated by DSC measurements, and a cis-trans isomerization was associated to it for the reasons given below. The heating rate of DSC run was 32°C/min, much higher than that used in thermal analysis, (9°C/min), so that the isomerization was prevented up to 200°C.

After scanning to 300°C temperature at which the isomerization was already accomplished, the sample was cooled down to 60°C in the sample holder and rescanned in the same condition (Fig. 5).

The first scanning shows an exothermal peak centered at 290°C (Fig. 5a). No endothermal effect was registered when the sample was cooled down (Fig. 5b) and no effect was exhibited at the second scanning (Fig. 5c) because of the irreversibility of the cis-trans isomerization. The DTA curves (Fig. 4) exhibit this effect at 260°C, in accord with the much lower heating rate of the analysis, but for the insoluble polymer fraction the transition is overlapped by decomposition. The same overlap was observed at higher heating

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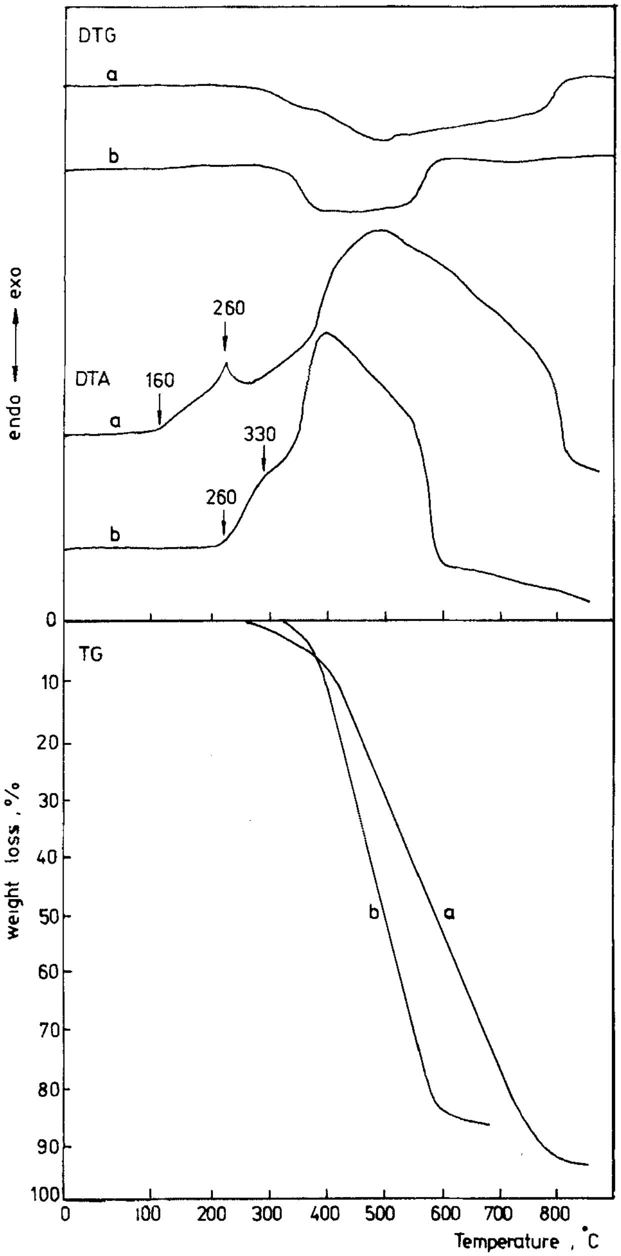

FIG. 4. DTG, DTA, and TG curves of PEA: (a) soluble fraction; (b) insoluble fraction. Heating rate, 9°C/min, air atmosphere.

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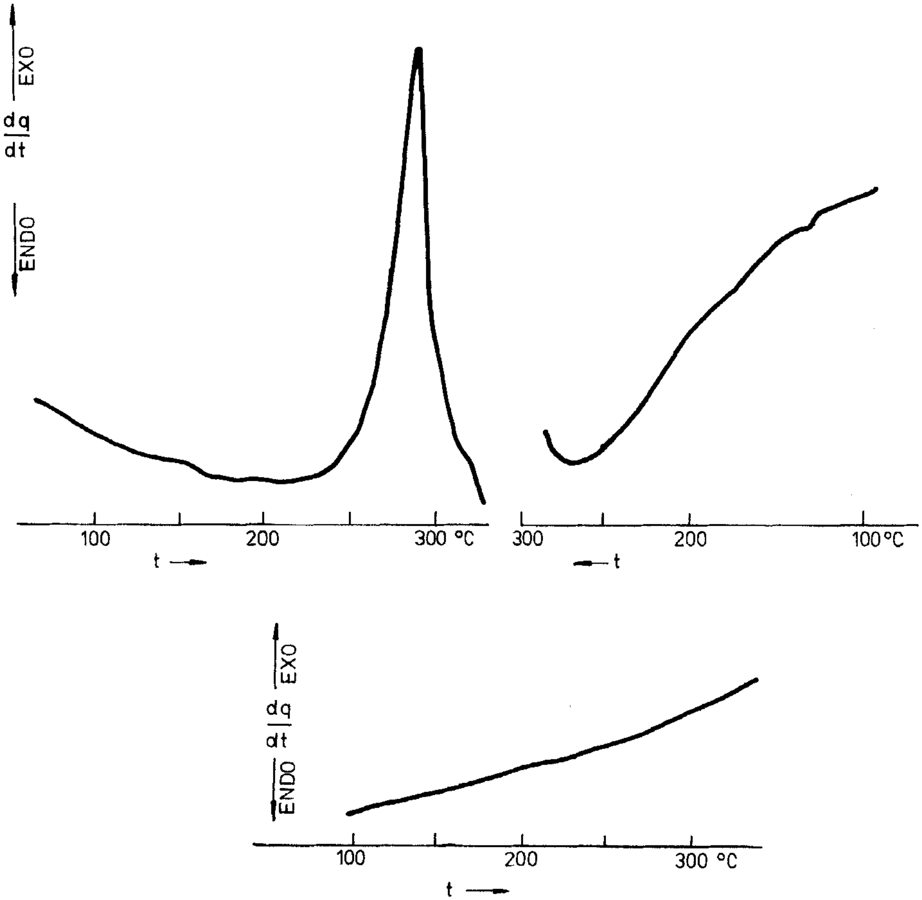

FIG. 5. DSC curves of PEA, soluble fraction: (a) first scanning; (b) cooling curve; (c) rescanning of the cooled sample. Scanning rate, 32°C/min, nitrogen atmosphere.

rates in DSC measurements. The DSC (DTA) temperature at which thermal decomposition starts to occur is 320°C (330°C). If the scan is stopped just before the decomposition, the insoluble fraction gains a high degree of solubility, in good agreement with the solubility of all-trans polymers derived from aromatic acetylenes [9, 10], indicating that the cis to trans isomerization already occurred to a great extent. The difficulties in isomerizing the insoluble PEA fraction,

i. e., no distinct peak and the overlapping of the isomerization with decomposition, in comparison with the soluble fraction, should be related to the high degree of packing of the cis-cisoidal structure which is unlikely to be disordered owing to the bulkiness of the substituent. The length of cis blocks (cisoidal or more favored transoidal) in soluble PEA has to be short and is interrupted by already isomerized units or dihydroanthracene units. The change of the structure caused by the thermal treatment is also supported by the change of the specific heat c_p after the isomerization, i. e., by the change of the slope of the rescanned DSC curve (Fig. 5).

The temperature of the cis-trans isomerization of substituted conjugated polymers is primarily dependent on the nature of the pendent substituent [10]. It ranges from 145°C for unsubstituted polyacetylene [11] to 216°C for poly-3-ethynylphenanthrene, with intermediate values for polyethynylferrocene and polyphenylacetylene at 157°C and 178°C, respectively [26]. For a given conjugated polyene, the ease of cis-trans isomerization much below the isomerization temperature is directly related to the volume of the substituent and with the degree of packing of the macromolecules. Small or medium aromatic substituent containing polyacetylenes, i. e., polyphenylacetylene and poly-α-ethynylnaphthalene, easily isomerize during polymerization at even low temperature if the temperature of the first catalyst active species-monomer contact is high [9] or during working-out of the polymer when the temperature could rise due to exothermic reactions [27]. Kleist and Byrd [28] reported that cis-rich polyacetylene having around 70% cis content isomerizes to trans polymer at even room temperature with a rate of cis to trans conversion of 5-6% per day. Obviously, the difficulty in the storage of the unsubstituted conjugated polyenes without isomerization to trans configuration led to the erroneous interpretation of obtaining of the most stable trans form only. Thus the synthetic α,ω-diphenylpolyenes, C_6H_5–$(CH{=}CH)_2$–C_6H_5, prepared by Kuhn [29] have been shown by x-ray diffraction to have all-trans configuration [30], much before the first report on the polymerization of acetylene to a linear chiefly trans polymer by Natta et al. [31].

The relative stability of cis-trans isomers may mean either thermochemical stability, measured by heat of formation, or thermodynamic stability, measured by free energy of formation. The difference in stability between cis and trans isomers may be expressed either as a difference in their enthalpy or as a difference in their free energy. The enthalpy change associated with the cis-trans isomerization in the solid state, however, seems not to be an independent phenomenon, and disorder in molecular arrangement and rearrangement are also included, for example in the thermal cis-trans isomerization of polyacetylene [11]. One good example could be found when the heat of combustion of trans-cinnamic acid (1040.9

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kcal/mole) is compared with that of the cis isomer in its three crystalline modifications, namely that melting at 68°C (1047.6 kcal/mole), that melting at 58°C (1045.2 kcal/mole, and that melting at 42°C (1043.8 kcal/mole) [30]. The respective differences in heats of combustion of 6.7, 4.3, and 2.9 kcal/mole, if taken as a difference in enthalpies of cis and trans isomers, should evidently be associated with the rigidity of the corresponding crystalline system as regards the solid state isomerization. Similarly, the exothermic phenomenon exhibited by DSC (DTA) diagrams of polyacetylene [28] and substituted conjugated polyenes [10], labeled as cis-rich isomers, should include, as pointed out by Ito et al. [11], besides the exothermic cis-trans isomerization an endothermic effect of in-plane disorder of molecular chains and an exothermic effect of in-plane disorder of molecular chains which precedes the isomerization, and a post-isomerization exothermic rearrangement. If the last two effects are not mutually balanced, the apparent heat of isomerization as measured by DSC (DTA) could be higher or lower than the real enthalpy changes. On the other hand, in the solid state the isomerization of cis units on the backbone takes place randomly and the already isomerized units could prevent the rotation of the neighboring units if the substituents are bulky. Even for polyacetylene 100% trans isomer was reported only from synthesis, while the trans polymer obtained by thermal isomerization of the cis-rich polyacetylene at 200°C had enough cis units to be detected by IR [11].

Taking into account these observations, the DTA (DSC) curves of PEA could be interpreted as follows. The (labeled cis-transoidal) soluble polymer fraction undergoes isomerization much more easily than the insoluble material labeled as cis-cisoidal polymer due to the loose packing of the chains of the former as compared with the relatively tight structure of the latter. Consequently, the disordering of the cis-cisoidal structure should be accompanied by a higher endothermic effect, and considering that the rearrangement of chains leads to the same geometrical isomer (trans) the overall heat of isomerization determined by DTA or DSC appears to be lower for the isomerization of cis-cisoidal polymer than for the isomerization of cis-transoidal polymer.

The DSC diagrams of insoluble materials obtained at the polymerization of substituted acetylenes, labeled as cis-cisoidal polymers [8, 10, 26], indeed show an endothermic effect which precedes the exothermic isomerization. Sometimes the endothermic rearrangement is evidenced by a shoulder, and if the interconversion temperature is high, overlapping of isomerization and decomposition occurs [26], as seen in Fig. 4.

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Accepted by editor July 5, 1978
Received for publication September 15, 1978

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